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SHORT TITLE OF WORK: "Quaternary Semiconductor Materials to Meet More Demanding Military Solid State Requirements"

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o DESCRIPTION OF PROGRESS

Since the previous report in this series (April 1, 1979), two manuscripts dealing with quantum-well InP-$In_{1-x}Ga_xP_{1-z}As_z$ heterostructures have been published and are included as reprints appended to this report. The first deals with using a quaternary quantum-well that collects photogenerated holes but not electrons to measure, by recombination-radiation energy, the valence-band discontinuity, ΔE_v, between InP and InGaPAs.[1] The basis for this measurement, which provides also $\Delta E_c \equiv \Delta E_g - \Delta E_v \sim 2E_v$, is illustrated by the inset shown in Fig.1 of Ref.1. In making this measurement in the InP-$In_{1-x}Ga_xP_{1-z}As_z$ system, we have identified an interesting new problem: a single quaternary quantum-well ceases to collect electrons somewhere in the size range of $L_z \sim 150$ Å compared to the binary GaAs at size $L_z \lesssim 80$ Å. The basic electron-phonon interaction in these two systems is comparable; thus we conclude, at least tentatively, that alloy disorder, and its effect on carrier energy loss via LO phonons, is the basis for this size difference in single-well electron collection. This problem will continue to receive further attention.

Reference 2, also appended to this report, demonstrates the importance of the electron-phonon interaction in quaternary quantum wells. Unlike a bulk III-V semiconductor sample ($L_z \geq 500$ Å), the step-like density of states of a quasi-two-dimensional quantum-well heterostructure aids the phonon participation in recombination and causes laser operation on phonon-sidebands below the confined-particle states.[2] This is an important development which applies also to CW, 300°K laser operation.

Photopumped continuous 300°K laser operation of LPE multiple-quantum-well In-$In_{1-x}Ga_xP_{1-z}As_z$ has been achieved at an excitation level of 7×10^3 W/cm^2 (or $J_{equiv} \sim 2.9 \times 10^3$ A/cm^2).[3] This laser operation has been observed two phonons below the lowest confined-particle transitions and well below E_g(InGaPAs). It is anticipated that as the quaternary LPE crystal growth process is improved further it will be possible to realize these same results in diodes. In the case of multiple-quantum-well $Al_xGa_{1-x}As$-GaAs laser diodes, the step-like density of states of the active region (and step-like distribution of the lower portion of the carrier distribution) leads to a much lower temperature dependence of the threshold current density.[4,5] This has been one of the vexing problems of conventional quaternary double heterojunctions, their high threshold-current temperature dependence. Based on the improved behavior of quantum-well $Al_xGa_{1-x}As$-GaAs laser diodes,[5] it is reasonable to assume that similar improvements will occur in quantum-well InP-$In_{1-x}Ga_xP_{1-z}As_z$ laser diodes. Also, the results of Ref.3 indicate that it should be possible to construct CW, 300°K multiple-quantum-well InP-$In_{1-x}Ga_xP_{1-z}As_z$ laser diodes, assuming it is possible to control the active region doping and keep it low enough to prevent screening of the electron-phonon interaction. (The electron-phonon interaction is important in scattering carriers to the lower energy states of the quantum-well active region.)

For detector applications of InGaAsP, relatively thick epitaxial layers are required compared to the thin active layers needed in double heterojunction lasers and the even thinner layers used in the quantum size effect structures just discussed. Because the lattice constant and bandgap of InGaAsP both change with variation in composition, it is essential that these thick layers have a constant composition. We have studied the influence of different growth techniques on the composition of the alloy layers.[6,7,8] This work shows that relatively thick (5-10 μm) constant composition InGaAsP layers can be grown by LPE at constant temperature using the diffusion-limited step-cooling growth technique with melt weights as small as 1.2g. Any of the other LPE growth techniques which involve growth with changing temperature (equilibrium-cooling, supercooling and two-phase-solution growth techniques) in general result in compositionally graded layers. Using the results of step-cooling growth experiments at different temperatures, it is possible to predict the amount of grading resulting during the other growth techniques from the temperature change during the growth of the epitaxial layers. While the grading observed may be insignificant for the growth of submicron layers in double heterostructure lasers, it can be very important in the growth of relatively thick layers for detector applications.

A more fundamental problem than grading of the epitaxial layer during growth under changing temperatures is grading at the interface of quaternary InP heterobarriers due to dissolution of a thin layer of the substrate or previously grown layer before growth is initiated.[9] Similar effects have been observed in AlGaAs/GaAs LPE growth,[10] but for this alloy system such dissolution of the substrate only results in a graded interface region with

a smoothly varying energy gap. The same grading at a quaternary/InP interface necessarily also results in lattice mismatch. The strain and/or dislocations due to this mismatch may be responsible for the high reverse bias leakage currents commonly observed in InGaAsP/InP photodiodes. Such an identification is consistent with both the observation that diffusion to form the p-n junction away from the metallurgical interface results in reduced leakage current,[11,12] and also with the low leakage currents obtained on Be-implanted diodes where the junction is formed entirely in the quaternary layer.[13.14] If the graded region with its associated lattice mismatch is responsible for the high leakage currents, the quaternary VPE growth techniques which make it possible to obtain abrupt lattice-matched interfaces may be even more important for detector applications than for heterojunction laser applications.

The study of the influence of different parameters on the growth of InP using the hydride growth technique has been continued. This work ~~will~~ is to be presented at the 156th Electrochemical Society Meeting, Los Angeles, 1979, and an abstract is included with the reprints/preprints at the end of this report. Because of moisture damage and contamination sustained during a flood this summer, it was decided to implement the new automatic gas flow control system described in the last report as soon as possible. The old system has been disassembled and heliarc welding on the new system is progressing rapidly.

Included at the end of this report are some reprints of papers that have been received since the last report and some preprints and abstracts of more recent work.

o CHANGE IN KEY PERSONNEL

There have been no changes in key personnel.

o SUMMARY OF SUBSTANTIVE INFORMATION DERIVED FROM SPECIAL EVENTS

Several interesting papers were presented at the Device Research Conference and Electronic Materials Conference held in Boulder at the end of June, and the vapor phase growth methods were discussed with several workers in the field. Reproducibility and abrupt transitions seem to be the major problems but it appears that adequate compositional control can be obtained using the Tylan mass flow controllers.

o PROBLEMS ENCOUNTERED AND/OR ANTICIPATED

A flash flood recently caused considerable moisture damage to the laboratories in the Electrical Engineering Research Laboratory. Because of the damage sustained, the vapor phase gas control system was dismantled and will be replaced with the automatic gas control system that is being assembled. The loss of the entire stock of the Electrical Engineering Electronics Storeroom may cause some delay because of the long delivery times of some items required in the new system.

o ACTION REQUIRED BY THE GOVERNMENT

A long term problem which could complicate extensions of this work and similar work in other laboratories is the availability of high-quality and reasonably priced InP substrate material. Varian, the only commercial U.S. supplier of InP substrates, has recently increased the price by 100% and the material is still not available--orders placed in June may be delivered in November or December but even this is not certain. The government should take steps to maintain a domestic supply of InP substrate material.

o FISCAL STATUS

(1) $374,913 is currently provided on contract.

(2) To date, $275,378 has been spent or committed.

(3) Funds required to complete work are estimated to be $99,535.

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